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ANTIMICROBIAL AGENT AND ANTIMICROBIAL POWDER HAVING  
IMPROVED POWDER FLUIDITY  
[RYUDOSEI NI SUGURERU KOKINZAI SOSEIBUTSU OYABI KOKINZAI  
FUNMATSU]

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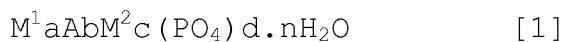
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OYABI KOKINZAI  
FUNMATSU

[What is claimed is]

1. An antimicrobial composition having improved powder fluidity, characterized in that it contains an antimicrobial powder represented by the following formula [1] and a fluidity improving powder that improves the powder fluidity of the antimicrobial powder.



[ $M^1$  represents at least one metal ion (the ionic valence is 1) selected from the group consisting of silver, zinc, tin, mercury, lead, iron, cobalt, nickel, manganese, arsenic, antimony, bismuth, barium, cadmium and chromium;  $A$  represents at least one metal ion (the ionic valence is  $m$ ) selected from the group consisting of an alkali metal ion, an alkaline earth metal ion, a hydrogen ion and an ammonium ion;  $M^2$  represents a tetravalent metal;  $n$  satisfies a formula:  $0 \leq n \leq 6$ ;  $a$  and  $b$  each represents a positive number; and  $c$  and  $d$  are each as follows:  $c$  is 2 and  $d$  is 3 when  $1a+mb=1$ , and  $c$  is 1 and  $d$  is 2 when  $1a+mb=2$ .]

2. The antimicrobial composition having improved powder fluidity according to Claim 1, characterized in that the fluidity improving powder is at least one material selected from the group consisting of calcium carbonate powder,

magnesium carbonate powder, amino acid modifiers and alkaline earth metal salts of a higher fatty acid.

3. The antimicrobial composition having improved powder fluidity according to Claim 1 or 2, characterized in that the sieve passing rate evaluated by the following testing method is 1.3 times or more as compared to the case without using the fluidity improving powder.

[Testing Method] 20 g of each sample is introduced into a 50 mL beaker, filled by tapping 10 times from a height of 1 cm, fed on a metallic mesh (aperture 4.5 mm, wire diameter 0.4 mm) from a height of 5 cm, and the weight of the sample passed through the metallic mesh is measured.

4. An antimicrobial powder having improved powder fluidity, characterized in that the surface of an antimicrobial powder represented by the above formula [1] is coated with a coupling agent in order to improve the powder fluidity.

5. The antimicrobial powder having improved powder fluidity according to Claim 4, characterized in that the coupling agent is a silane coupling agent.

6. The antimicrobial powder having improved powder fluidity according to Claim 4 or 5, characterized in that the sieve passing rate evaluated by the following testing method is 1.3 times or more as compared to the case where the surface is not coated with the coupling agent.

[Testing Method] 20 g of each sample is introduced into a 50 mL beaker, filled by tapping 10 times from a height of 1 cm, fed on a metallic mesh (aperture 4.5 mm, wire diameter 0.4 mm) from a height of 5 cm, and the weight of the sample passed through the metallic mesh is measured..

7. An antimicrobial composition having improved powder fluidity, characterized in that it contains the antimicrobial powder according to any of Claims 4 through 6 and a fluidity improving powder that improves the powder fluidity of the antimicrobial powder.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention] The present invention relates to an antimicrobial agent or powder having improved powder fluidity. The present invention can be used in a technical field in which a screened powder obtained by passing such an antimicrobial agent or powder through a mesh is used, such as a field in which resins, ceramics or fibers are formed.

[0002]

[Prior Art] It has been conventionally conducted that an antimicrobial agent or powder is passed though a mesh, the resulting screened powder is incorporated into other raw

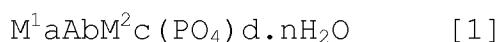
material powder, such as resin powder and ceramic powder, and the resulting composition is formed.

[0003]

[Problems to be Solved by the Invention] When the antimicrobial composition or powder is passed through a mesh, the powder might not pass through the mesh but remain on it. In this case, the operator must let the remaining powder through the mesh manually, increasing the workload of the operator. Hence, there is a demand for developing an antimicrobial composition or powder which readily passes through a mesh. The present invention was completed in view of the above-described situation and intends to provide an antimicrobial composition and an antimicrobial powder which readily pass through a mesh.

[0004]

[Means of Solving the Problems] The antimicrobial composition having improved powder fluidity according to the first aspect of the present invention ("the inventive antimicrobial composition", hereinafter) is characterized in that it contains an antimicrobial powder represented by the following formula [1] and a fluidity improving powder that improves the powder fluidity of the antimicrobial powder.



[ $M^1$  represents at least one metal ion (the ionic valence is 1) selected from the group consisting of silver, zinc, tin, mercury, lead, iron, cobalt, nickel, manganese, arsenic, antimony, bismuth, barium, cadmium and chromium;  $A$  represents at least one metal ion (the ionic valence is m) selected from the group consisting of an alkali metal ion, an alkaline earth metal ion, a hydrogen ion and an ammonium ion;  $M^2$  represents a tetravalent metal; n satisfies a formula:  $0 \leq n \leq 6$ ; a and b each represents a positive number; and c and d are each as follows: c is 2 and d is 3 when  $1a+mb=1$ , and c is 1 and d is 2 when  $1a+mb=2$ .]

[0005] The antimicrobial powder having improved powder fluidity according to the fourth aspect of the present invention ("the inventive microbial powder", hereinafter) is characterized in that the surface of an antimicrobial powder represented by the above formula [1] is coated with a coupling agent in order to improve the powder fluidity.

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The antimicrobial composition having improved powder fluidity according to the seventh aspect of the present invention ("the inventive antimicrobial composition", hereinafter) is characterized in that it contains the antimicrobial powder according to any of Claims 4 through 6

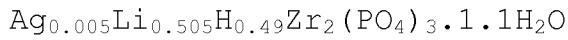
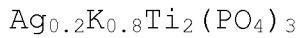
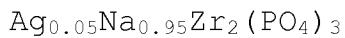
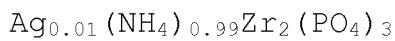
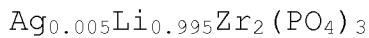
and a fluidity improving powder that improves the powder fluidity of the antimicrobial powder. Further, in the first, fourth or seventh aspect of the present invention, other additive agents (e.g., antimicrobial improving agents, weatherability improving agents and fillers) which do not work in improving the powder fluidity of the antimicrobial powder can also be incorporated. Both ceramic additive agents and resin additive agents can be used, with ceramic additive agents being generally used.

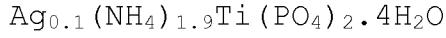
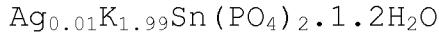
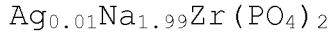
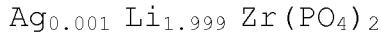
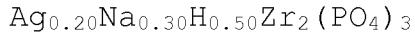
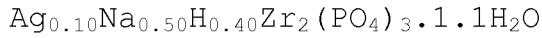
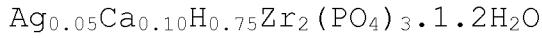
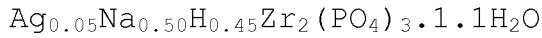
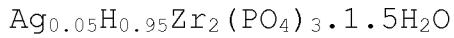
[0006] The phosphate, which is the "antimicrobial powder" represented by the above formula [1], is a crystalline compound which is amorphous or belongs to the space group R3c and which has coefficients c=2 and d=3 in the case of  $1a+mb=1$ . The ions constituting the compound form a three-dimensional network structure. Further, the phosphate can be a compound which has coefficients c=1 and d=2 in the case of  $1a+mb=2$  and is amorphous or the ions constituting the compound form a layer structure. The phosphate used in the present invention can be preferably the composition which is amorphous or belongs to the space group R3c and which has coefficients c=2 and d=3 in the case of  $1a+mb=1$ , with the ions constituting the compound forming a three-dimensional network structure from the standpoint where the discoloration by exposure to sunlight can be inhibited.

[0007] The element "M<sup>1</sup>" in the above formula [1] is known as a metal having mildewproofing properties, antimicrobic properties and seaweedproofing properties, with silver being most preferred. This is because silver is highly safe and can improve mildewproofing properties, antimicrobic properties and seaweedproofing properties.

[0008] Preferred specific examples of the element "A" in the above formula [1] include alkali metal ions, such as lithium, sodium and potassium, and alkaline earth metal ions, such as magnesium and calcium. Of these, from the standpoint of the stability of the compound and the low-cost availability, lithium ion, sodium ion, hydrogen ion and ammonium ion are preferred. The element "M<sup>2</sup>" is a tetravalent metal, known specific examples of which include zirconium, titanium and tin. Of these, from the standpoint of the safety of the compound, zirconium and titanium are particularly preferred.

[0009] Specific examples of the phosphate of the above formula [1] are as follows:





Further, Ag in the above formula can be substituted with Zn, Mn, Ni, Pb, Hg, Sn or Cu while the charge amount of such a metal is being adjusted to the charge amount of silver per mole of the above compound.

[0010] In order to obtain the mildewproofing properties, antimicrobial properties and seaweedproofing properties, the value of "a" in the above formula [1] can be preferably high; however, if the value of "a" is 0.001 or higher, sufficient antimicrobial properties may not be obtained; whereas if the value of "a" is less than 0.01, the antimicrobial properties may not be maintained for an

extended period of time and the economical efficiency may be impaired; therefore the value of "a" is preferably 0.01 or higher and 0.5 or less.

[0011] The phosphate which is an antimicrobial powder used in the present invention is stable to exposure to heat and light, can therefore maintain the structure and composition even by heating it at a temperature of 500 degrees Celsius, 800 to 1100 degrees Celsius in some cases, and prevents discoloration that can be caused by exposure to ultraviolet light. Further, the phosphate prevents the deformation of the skeletal structure even in an acidic solution. Hence, the process and storage in obtaining various formed products are not limited and heating temperature and light blocking conditions during use are also not limited unlike conventional antimicrobial agents. In synthesizing the phosphate, which is the inventive antimicrobial powder, methods that can be applied include various conventional dry processes, wet processes and hydrothermal methods.

[0012] The term "fluidity improving powder" used herein refers to any powdered materials which improve the powder fluidity of the antimicrobial powder. Examples of such powder materials include various powders of calcium carbonate, magnesium carbonate, amino acid modifiers (e.g., monoaminodicarboxylic acid having an alkyl group having 6

to 20 carbon atoms, and the monoesters or diesters thereof), alkaline earth metal salts of a higher fatty acid (e.g., magnesium stearate, calcium stearate, magnesium oleate and calcium oleate), alumina, aluminum hydroxide, aluminum potassium sulfate, MgO, calcium phosphates [e.g., Ca<sub>3</sub>(PO<sub>4</sub>) and CaHPO<sub>4</sub>],

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talc, titanium oxide, colloidal silica and aluminum silicate hydrates. Of these fluidity improving powders, particularly preferred examples include alkaline earth metal carbonates (e.g., calcium carbonate powder and magnesium carbonate powder), amino acid modifiers and alkaline earth metal salts of a higher fatty acid (e.g., magnesium stearate, calcium stearate, magnesium oleate and calcium oleate). These fluidity improving powders can be used alone or in combination of two or more. The desired proportion of the fluidity improving powder may vary depending on the type, but in the case of a fluidity improving powder having good fluidity by itself, such as calcium carbonate, the proportion is 5 to 200 parts by weight as against 100 parts by weight of the antimicrobial powder. If the proportion is less than 5 parts by weight, a sufficient fluidity improving effect may not be obtained, whereas if the proportion exceeds 200 parts by weight, a

large amount of antimicrobial composition must be added to a resin or a coating solution in order to obtain a sufficient fluidity improving effect, resulting in the original physical properties of the resin or the coating solution being impaired. In the case where the fluidity improving powder is a surface modifying powder which improves the fluidity by modifying the surface of the powder which is in contact with such a modifying powder, such as amino acid modifiers or alkaline earth metal salts of a higher fatty acid, the desired proportion is 0.1 to 10 parts by weight as against 100 parts by weight of the antimicrobial powder. If the proportion is less than 0.1 parts by weight, a sufficient fluidity improving effect may not be obtained, whereas if the proportion exceeds 10 parts by weight, conversely, the fluidity may be impaired.

[0013] The term "coupling agents" used herein refers to any materials which improve the fluidity of the powder.

Examples of such coupling agents include silane coupling agents (organic silicon compounds), organic aluminum compounds and organic titanium compounds. Examples of such organic silicon compounds include: (1) vinyl compounds, such as vinyltrimethoxysilane and vinyltriethoxysilane; (2) amino compounds, such as N-(2-aminoethyl)3-aminopropylmethyldimethoxysilane, N-(2-aminoethyl)3-

aminopropyltrimethoxysilane and 3-aminopropyltriethoxysilane; (3) epoxy compounds, such as 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropylmethyldimethoxysilane and 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane; (4) chloro compounds, such as 3-chloropropylmethyldimethoxysilane, 3-chloropropyltrimethoxysilane, trimethylchrolosilane, dimethyldichlorosilane and methyltrichlorosilane; (5) methacryloxy compounds, such as 3-methacryloxypropyltrimethoxysilane; (6) mercapto compounds, such as 3-mercaptopropyltrimethoxysilane; (7) cation compounds, such as N-[2-(vinylbenzylamino)ethyl]-3-aminopropyltrimethoxysilane hydrochloride; and (8) silazane compounds, such as hexamethyldisilazane. Examples of such organic aluminum compounds include acetalkoxyaluminum diisopropylate, mono-s-butoxyaluminum diisopropylate, aluminum ethylate, aluminum ethyl acetoacetate diisopropylate, aluminum tris(ethyl acetoacetate), and aluminum bisethyl acetyl acetate monoacetyl acetonate. Examples of such organic titanium compounds include tetraisopropoxytitanium, tetra-n-butoxysilane, tetrastearoxytitanium, alkoxy polytitanyl acrylate, diisopropoxy-bis(acetylacetato)titanium, hydroxy-bis-(lactate)titanium, and isopropyltriisostearoisotitanate. Of

these, silane coupling agents (organic silicon compounds) are particularly preferred as a coupling agent for the present invention.

[0014] When the surface of the phosphate is treated with a coupling agent, the phosphate can be preferably coated with 0.01 to 5 parts by weight of the coupling agent as against 100 parts by weight of the phosphate. Such coating can be conducted by directly applying the coupling agent to the phosphate or by diluting a specific amount of the coupling agent in an organic solvent or water and applying the resulting solution to the phosphate. Methods for the coating are not particularly restricted but any conventional treatments for inorganic powder, such as dry method, wet method, spraying method and gas method, can be used. The sieve passing rate of the inventive microbial composition or powder is 1.3 times or more as compared to the case where the above-described fluidity improving powder is not added or the above-described coupling agent is not applied (to the antimicrobial powder itself). The method for testing the sieve passing rate is as follows. Specifically, 20 g of a sample is introduced into a 50 mL beaker, filled by tapping 10 times from a height of 1 cm, fed on a metallic mesh (aperture 4.5 mm, wire diameter 0.4

mm) from a height of 5 cm, and the weight of the sample passed through the metallic mesh is measured.

[Modes of Implementing the Invention]

[0015] The present invention is described in greater detail with reference to embodiment below.

Embodiment 1

In the present embodiment, types of the fluidity improving powder ("additives", hereinafter) were investigated.

According to the types and proportions of the additive shown in Table 1, the powder fluidity was investigated by the following sieve passing test. The unit of the proportion is "wt%".

[0016]

[Table 1]

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Samp le No.	Proportion of antimicrobial powder (%)	Additives and the proportion (%)	Sieve passing rate (%)	Ratio of the sieve passing rate to blank
1	100	(blank) 0	44.6	-
2	90	CaCO <sub>3</sub> powder 10	69.6	1.56
3	90	Al <sub>2</sub> O <sub>3</sub> powder 10	50.0	1.12
4	90	Al(OH) <sub>3</sub> powder 10	53.4	1.20
5	90	AIK(SO <sub>4</sub> ) <sub>2</sub> powder A 10	47.5	1.07
6	90	AIK(SO <sub>4</sub> ) <sub>2</sub> powder B	50.8	1.14
7	98	Amino acid modifier 2	59.4	1.39
8	98	Magnesium stearate powder 2	59.2	1.33
9	Antimicrobial powder treated with a silane coupling agent		62.1	1.33

[0017] The antimicrobial powders used in the present embodiment were Novaron AGZ330 (manufactured by Toagosei Co., Ltd; average particle diameter: 1.3 µm) except for No.

9, and Novaron AG300 (manufactured by Toagosei Co., Ltd; average particle diameter: 0.9  $\mu\text{m}$ ) was used for No. 9.

[0018] In Table 1, "calcium carbonate powder" used was "Calfine 200M" (manufactured by Maruo Calcium Co., Ltd; average particle diameter: 9.7  $\mu\text{m}$ ),  $\text{Al}_2\text{O}_3$  powder  $\text{Al}(\text{OH})_3$  powder used were reagents (average particle diameter: 33  $\mu\text{m}$  and 56  $\mu\text{m}$ ),  $\text{AlK}(\text{SO}_4)_2$  powder A used was "Taiace K20" (Taimei Chemicals Co., Ltd; average particle diameter: 5  $\mu\text{m}$ ), and  $\text{AlK}(\text{SO}_4)_2$  powder B used as "Taiace K150" (Taimei Chemicals Co., Ltd; average particle diameter: 30  $\mu\text{m}$ ). Amino acid modifier used as "Feimex" (Ajinomoto Co., Inc.) and had a chemical formula:  $\text{RN}(\text{H})\text{CH}(\text{CH}_2\text{CO}_2\text{R})\text{CO}_2\text{H}$  (R represents a lauryl group and a stearyl group). "Magnesium stearate powder" used was "SM-P" (manufactured by Sakai Chemical Industry Co., Ltd.) "Silane coupling-treated powder" used was obtained by treating the powder by using a silane coupling agent "KBM-503" (manufactured by Shin-Etsu Chemical Co., Ltd.) This silane coupling treatment was adding approximately 0.1 g of the silane coupling agent to 100 g of a predetermined powder, stirring and heating the mixture, thereby forming a coating on the surface.

[0019] [Sieve passing test] 20 g of each sample was introduced into a 50 mL beaker, and was filled by tapping 10 times from a height of 1 cm. The resulting sample was

fed on a metallic mesh (aperture 4.5 mm, wire diameter 0.4 mm) from a height of 5 cm, and the weight of the sample passed through the metallic mesh was measured. Since the passing rate may vary by vibration, the test was conducted without vibration.

[0020] The test results are shown in Table 1. According to the results, the most preferred results were obtained from calcium carbonate powder (sieve passing ratio: 1.56 as against blank), amino acid modifier composition (sieve passing ratio: 1.39), magnesium stearate powder (sieve passing ratio: 1.33) and silane coupling-treated powder (sieve passing ratio: 1.33). Of these, calcium carbonate powder is particularly preferred. For this reason, an additive having a carbonate and a carboxyl group was found to be particularly preferred. The Sample containing  $\text{Al}_2\text{O}_3$  powder,  $\text{Al}(\text{OH})_3$  powder,  $\text{AlK}(\text{SO}_4)_2$  powder A or  $\text{AlK}(\text{SO}_4)_2$  powder B showed a better sieve passing rate (sieve passing ratios: 1.12, 1.20, 1.07 and 1.14 respectively) than an additive without containing these additives (i.e., sample No.1), although the rate was still lower than the above-mentioned samples.

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[0021] Embodiment 2

In the present embodiment, the proportion of three additives which showed a significant fluidity improving effect in Embodiment 1 was investigated. The additives were, as shown in Table 2, calcium carbonate powder (20%, 40%), amino acid modifier (4%, 6%) and magnesium stearate powder (4%, 6%). The testing method was the same as Embodiment 1. The results are shown in Table 2.

[0022]

[Table 2]

Sample No.	Proportion of antimicrobial powder (%)	Additives and the proportion (%)	Sieve passing rate (%)	Ratio of the sieve passing rate to blank
10	80	CaCO <sub>3</sub> powder 20	73.3	1.64
11	60	CaCO <sub>3</sub> powder 40	78.7	1.76
12	96	Amino acid modifier 4	63.0	1.42
13	94	Amino acid modifier 6	75.8	1.70
14	96	Magnesium stearate powder 4	73.0	1.64
15	94	Magnesium stearate powder 6	65.8	1.48

[0023] According to the results, in the case of calcium carbonate powder, the sieve passing rate increased as the proportion increased to 10% (as shown in Table 1), 20% and 40%. Therefore, an excellent performance can be obtained within the proportion range of 10 to 40% (in particular, 20 to 40%). In the case of the amino acid modifier, the sieve passing rate increased as the proportion increased to 2%, 4% and 6%. Therefore, an excellent performance can be obtained within the proportion range of 2 to 6% (in

particular, 4 to 6%). In the case of magnesium stearate powder, the highest sieve passing rate was obtained at a proportion of 4%, and the increase in the sieve passing rate decreased at a proportion of 6%; hence, the proportion was considered to have an appropriate value. Therefore, an excellent performance can be obtained within the proportion range of 2 to 6%, and in particular, approximately 4% (3 to 5%). The present invention is not restricted to the above-described embodiments, but can be modified according to the intended use and objectives without departing the scope of the present invention.

[0024]

[Effect of the Invention] The inventive antimicrobial composition or powder, which can be readily passed through a sieve when it is screened, can be prevented from remaining on the sieve. Therefore, increasing excessive load on the operator can be prevented, and the screening process can be automatically or continuously conducted.